

Replica Molding Using Polymeric Materials: A Practical Step Toward Nanomanufacturing

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This paper describes a practical procedure-replica molding of organic polymers against masters having nanometer-sized relief features on their surfaces-to fabricate nanostructures (that is, structures with feature sizes ≤ 100 nm in dimension). (1) Nanostructures are increasingly important as components in new types of electronic, magnetic and optical devices. They are now ordinarily fabricated by advanced lithographic techniques such as e-beam writing, X-ray lithography and proximal-probe lithography.(2) These techniques are flexible and capable of providing very small features, but their development into methods for generating large numbers of nanostructures at low cost will require great ingenuity.(3) The manufacturing of nanostructures, that is, the making of multiple copies reproducibility, rapidly and at low cost, will require new procedures; methods using organic polymers, for example, imprinting (or embossing) using a rigid master,(4) and polymerization in the nanometer-sized pores of a membrane,(5) have been demonstrated for this purpose.

The procedure reported here is based on replica molding using organic polymers, a technique that has found widespread applications in the manufacturing of micrometer-sized structures such as diffraction gratings,(6) compact disks,(7) and microtools.(8,9) Here, we extend replica molding to the fabrication of nanometer-sized structures. Replication against elastomeric (rather than rigid) masters enormously increases the ease of separating the master and the replica, protects the fragile structures during separation, and minimizes damage to the master. Moreover, extension of this procedure-replica molding against an elastomeric master while bent mechanically-allows the fabrication of nanostructures with a level of control over the form and size of the pattern that is not possible with existing techniques.(10,11)

Figure 1A shows the procedure schematically. A liquid prepolymer of poly(dimethylsiloxane) (PDMS) is cast against an original master whose surface has been patterned with nanometer-sized relief structures, made using advanced lithographic techniques; these features could be SiO_2 , Si_3N_4 , metals, or photoresists, for example, poly(methylmethacrylate) (PMMA). After curing, the cross linked and elastomeric PDMS is carefully peeled from the master; its surface replicates the relief nanostructures on the surface of the original master. The nanostructures present on the PDMS replica are, in turn, re-replicated using a rigid organic polymer, for example, an photochemically curable polyurethane (PU), to produce polymeric nanostructures very similar to (or indistinguishable from) those on the surface of the original master. Replica molding of the PU against a PDMS master could also be carried out while the PDMS master is bent mechanically (see Fig. 1B); this procedure generates PU nanostructures having smaller feature sizes than those on the original master.

Figure 2 shows atomic force microscopy (AFM) images of a Cr master, (12) its PDMS and PU replicas made from the PDMS master. The most important feature of this replicated PU nanostructure is its replication of nanometer-scale features. The heights of the Cr lines on the original Cr masters are ~ 13 nm, and the heights of the PU lines are ~ 8 nm. These images demonstrate that within our ability to compare similar structures, the nanostructures are

faithfully reproduced over a large area.

We also monitored the reduction in quality in the nanostructures on the original master and the PU replicas. Figure 3A shows an AFM image of a gold master before it was used to cast PDMS masters; Figure 3B shows an AFM image of this gold master after it has been used to cast seven PDMS replicas. No observable reduction in quality was found in these gold nanostructures. Figure 3C shows AFM image of the first PU replica generated from the fourth PDMS master cast from this gold master; Figure 3D is an AFM image of the sixth PU replica cast from the fifth PDMS master. Again, no obvious change in quality was observed for these nanostructures on the PU replicas. This procedure, therefore, has the capability of generating multiple copies of nanostructures starting from a single master. Both the simplicity and low cost of this procedure confirm its potential use in nanomanufacturing.

Figure 3E shows an AFM image of another gold master having features of ~ 50 nm in size; Figure 3F shows an AFM image of a PU replica cast from a PDMS master (cast from this gold master) while it was bent mechanically (see Figure 1B). The dimension of the features was reduced from ~ 50 nm to ~ 30 nm in this process.

This work demonstrated a practical protocol based on replica molding for the fabrication of structures in organic polymers with lateral dimensions as small as ~ 30 nm. Recently, Chou and co-workers demonstrated a related procedure - embossing in organic polymers - that generates polymeric features with dimensions of ~ 25 nm. (4) These demonstrations make it clear that the fabrication of multiple copies of nanostructured organic polymers is a practical reality. These types of replication procedures provide a conceptual route to nanomanufacturing: conventional highresolution lithographic techniques would be used to make masters, and these structures would then be replicated into organic polymers. The ability to make both positive and negative replicas, and to modify the dimensions and shapes of features present on elastomeric masters by mechanical deformation, adds further flexibility to this methodology. Using nanostructures to generate electronically, optically, and magnetically functional components and systems will require a development of new technologies; the present limiting step, i.e. the mass production of nanostructures, finds a range of potential solutions in this work.